

Effect of Intra-molecular Disorder and Inter-molecular Electronic Interactions on the Electronic Structure of Poly-*p*-Phenylene Vinylene (PPV)

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We investigate the role of intra-molecular conformational disorder and inter-molecular electronic interactions on the electronic structure of disorder clusters of poly-*p*-phenylene vinylene (PPV) oligomers. Classical molecular dynamics is used to determine probable molecular geometries, and first-principle density functional theory (DFT) calculations are used to determine electronic structure. Intra-molecular and inter-molecular effects are disentangled by contrasting results for densely packed oligomer clusters with those for ensembles of isolated oligomers with the same intra-molecular geometries. We find that electron trap states are induced primarily by intra-molecular configuration disorder, while the hole trap states are generated primarily from inter-molecular electronic interactions.

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The emergence of organic electronic devices, including light emitting diodes and field effect transistors, fabricated from conjugated polymers such as poly-*p*-phenylene vinylene (PPV) [1] has stimulated research into the electrical and optical properties of these semi-conducting polymers. A theoretical description of these electronic materials is challenging because they are highly disordered and strong interactions between molecules occurring in the condensed phase of the materials are very important in determining their properties. Despite extensive experimental [2] and theoretical research [3], there is still a limited understanding of these strongly interacting disordered materials. In this Letter, we use a combination of classical molecular dynamics (MD) and density functional theory (DFT) to investigate the electronic structure of densely packed clusters of PPV oligomers. Classical MD is used to determine statistically probable molecular geometries for large clusters of PPV oligomers, and DFT calculations are used to determine the electronic structure of the clusters. The effect of intra-molecular configurational disorder and of inter-molecular electronic interactions on the electronic structure are disentangled by contrasting the calculated density of states and molecular orbitals for a densely packed oligomer cluster with that for an ensemble of isolated oligomers with the same intra-molecular geometries as the oligomers in the clusters.

Statistically probable geometries of disordered clusters of PPV oligomers were simulated using classical MD. To isolate the effect of configurational disorder, we specifically consider clusters of five-ring PPV oligomers as studied experimentally in Ref [4]. Figure 1 shows the structure of the five-ring PPV oligomer (Fig. 1a), a crystal [4] of ordered oligomers (Fig. 1b), and an example of a disordered oligomer cluster from the MD simulations (Fig. 1c). The unit cell used for the MD simulations and DFT calculations consisted of 12 five-ring oligomers, a total of 816 atoms.

Single crystals of PPV oligomers have been grown and

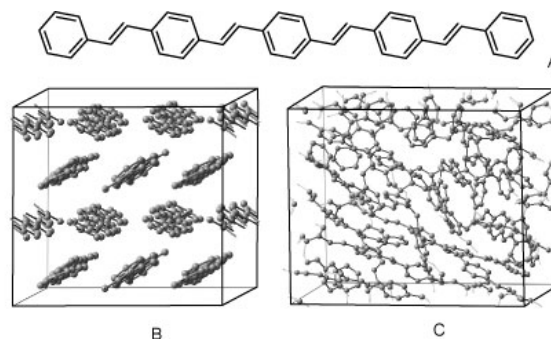


FIG. 1: (A) Molecular structure of the ordered oligomer; (B) Experimental crystal structure [4]. (C) Molecular structure of an oligomer cluster determined from the MD simulation. Hydrogen atoms are not shown for clarity.

structurally characterized [4]. Thin films of the polymer consist of small ordered regions, with a structure similar to that of the crystalline oligomers, separated by disordered regions. The MD simulations are meant to describe the disordered regions. Substituted versions of PPV such as poly [2-methoxy, 5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) are frequently used in organic electronics. In these materials the substituted side groups, added primarily for processing reasons, are saturated and do not play a direct role in the electronic structure of the materials. However, in a condensed phase the substituted side groups tend to separate the conjugated segments of different molecules and thus reduce inter-molecular electronic interactions compared to pristine conjugated polymers. Thus a combination of the crystal and an ensemble of disordered oligomer clusters serves as a model for the electronic structure of pristine PPV. And a combination of the isolated ordered oligomer and an ensemble of isolated disordered oligomers serves as a model for the electronic structure of substituted PPVs.

A statistical sample of molecular geometries for the

disordered PPV oligomers was generated by simulated annealing using periodic-boundary-condition MD with a modified MM3-2000 force field [5], as implemented in the Tinker code [6]. Because the conventional MM3-2000 force field does not distinguish between single and double C-C bonds, a new term was added. This new term was chosen to reproduce the C=C double bond force constant and bond distance obtained from hybrid density functional calculations (B3LYP). The new force term was used in linking the vinyl group and the aromatic sp^2 carbon atoms and the usual MM3-2000 force field was used for the remaining carbons. This combination of force field terms produced the difference between averaged length of all single bonds and double bonds of 0.19 Å. This is usually referred as the bond length alteration factor. In the simulated annealing calculations, the PPV oligomers were initially distributed randomly at extremely low density ($\rho \approx 0.01 \text{ g/cm}^3$), heated to 10,000K, and then pressure was applied to reach the experimental density of 1.25 g/cm^3 . At this density the volume of the simulation cell was kept constant and the temperature cooled to zero K. Molecular geometries were extracted after the experimental density and zero K were reached, and statistical samples were generated by repeating the simulated annealing procedure.

The electronic structure of the crystalline and disordered oligomer configurations were calculated using periodic-boundary-condition density functional theory (DFT) at the generalized gradient approximation (GGA) level of approximation, using the PW91 functional [7]. The DFT calculations were performed at fixed geometries, determined from the MD simulations using the VASP code [8], VASP with the projector-augmented wave (PAW) scheme [9]. Due to the large size of the simulation cells (typically at least 20 Å on each side) Γ -point sampling of the Brillouin zone was adequate. This point was explicitly verified by adding an extra sampling k-point in each direction. Use of the GGA approximation leads to an underestimate of the energy gap, typical of pure DFT calculations. However, we are primarily interested in electronic states near the HOMO and LUMO energy levels separately and not in the absolute value of the energy gap.

The upper panel of Fig. 2 shows calculated energy levels for the ideal crystal (far left) and for 14 different disordered oligomer clusters, labelled S1-S14, whose geometries were determined from the MD simulations. The lower panel of Fig. 2 shows calculated energy levels for the ensemble of 12 isolated oligomers making up the oligomer clusters in the corresponding column of the upper panel. The zero of energy was set to the middle of the energy gap of the perfect crystal (upper panel) or of the undistorted oligomer (lower panel). The effect of disorder on the electronic structure of the densely packed oligomer clusters can be separated into two components: intra-molecular disorder and inter-molecular electronic

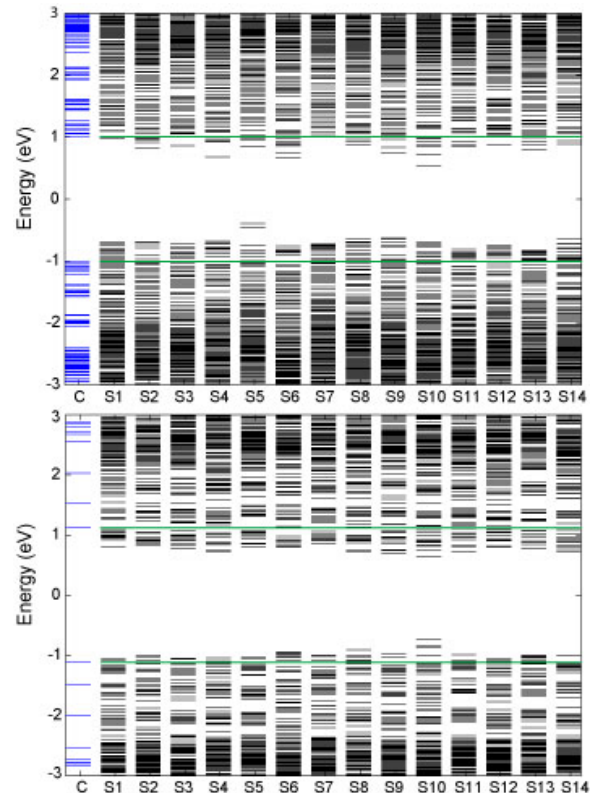


FIG. 2: Energy level diagrams from the DFT calculations. The upper panel shows results for the ideal crystal (far left) and for 14 disordered oligomer clusters whose geometry was determined from the MD calculations; the lower panel shows results for an isolated ordered oligomer (far left) and an ensemble of 12 isolated oligomers with the same molecular geometries as in the corresponding column of the upper panel.

interactions. Intra-molecular disorder is due to conformational deformations, resulting from the oligomers not being straight and planar but, kinked and twisted. These geometrical distortions interrupt the conjugation of the π orbitals causing the electronic states to be more localized. Inter-molecular interactions vary in the densely packed oligomer clusters because of differences in the local packing of the oligomers. The inter-molecular π - π interactions depend strongly on the relative orientation of neighboring oligomers. To disentangle the effects of intra-molecular conformational disorder and the inter-molecular interaction effects on the energy level diagram, the electronic structure of each isolated oligomer in a cluster was computed independently (see lower panel of Fig. 2). The lack of repulsion among electron densities stabilizes the occupied levels showing that the hole traps originate from the packing of the oligomers.

Panels A-D of Fig. 3 show calculated density of states for: (A) the ideal crystal, (B) oligomer clusters S4, and (C) S5, and (D) the ensemble averaged density of states for oligomer clusters S1 - S14. Panels E-H of Fig. 3

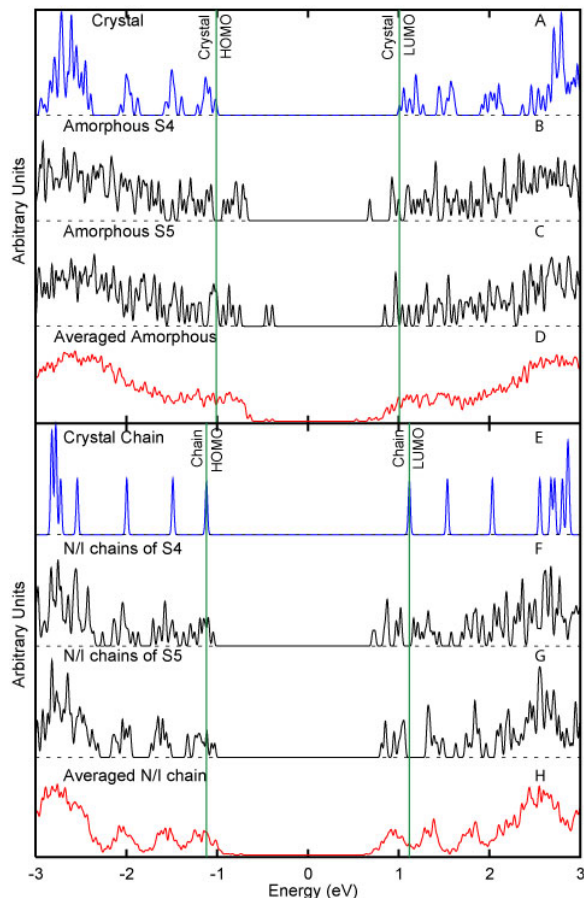


FIG. 3: Calculated density of states for: (A) the ideal crystal; (B) disordered cluster S4; (C) disordered cluster S5; (D) the ensemble average of clusters S1-S14; (E) the ordered oligomer in the crystal; (F) the 12 isolated oligomers in cluster S4; (G) the 12 isolated oligomers in cluster S5; (H) the ensemble average of isolated oligomers in clusters S1-S14. Note that 'green lines' denote different energy gaps in top panels A-D vs. bottom panels E-H.

show calculated density of states for: (E) the undistorted oligomer in the ideal crystal, (F) the 12 isolated oligomers in clusters S4, and (G) S5, and (H) the ensemble averaged density of states for the isolated oligomers in clusters S1 - S14. The density of states have been broadened using a Gaussian with full width at half maximum of 0.0136 eV. The zero of energy was set to the middle of the energy gap of the perfect crystal (panels A-D) or of the undistorted oligomer (panels E-H).

The density of states for the isolated undistorted oligomer (see, Fig. 3E) consists of a series of discrete states. In the crystal (see Fig. 3A), these discrete states are broadened into bands because of inter-molecular electronic interactions. Because of these inter-molecular interactions, the energy gap of the crystal is smaller than that of the isolated undistorted oligomer. The packing pattern in the crystal is of the herringbone type, a common arrangement for conjugated oligomers with-

out substitutions [10]. Inter-molecular electronic interactions in crystals with the herringbone structure are relatively small due to the weak π - π overlap between oligomers (see Fig. 1B). In the ensemble of distorted but isolated oligomers (see Fig. 3H), the discrete lines of the undistorted oligomer are broadened by the statistical distribution of molecular distortions. Comparing Fig. 3E with Fig. 3H shows that this broadening in the valence states is nearly symmetric about the position of the corresponding valence state in the undistorted oligomer. In contrast, the distortions both broaden and shift to lower energy the conduction states compared to the corresponding conduction state in the undistorted oligomer. This can be traced to specific intra-molecular interactions. The occurrence of cis-configurations about the vinylenic linkages in some of the distorted oligomers tends to symmetrically reduce the HOMO-LUMO energy gap, whereas distortions of the bond lengths and angles in the vinylenic linkages in some distorted oligomers (either cis or trans configurations) tend to lower both the HOMO and LUMO energies. A combination of these two effects leads to the nearly symmetric broadening of the unoccupied levels seen in Fig. 3H. Contrasting Fig. 3A and Fig. 3D, we see stronger inter-molecular electronic interactions in the disordered oligomer clusters than in the crystal. This occurs because the π - π interactions are comparatively weak in the herringbone crystal structure where adjacent oligomer planes do not strongly overlap, but can be much larger in the disordered phase where adjacent oligomer planes can overlap strongly. Comparing the ensemble averaged results in Fig. 3D and Fig. 3H (and the corresponding single cluster cases (panel B with F; and panel C with G)) shows that inter-molecular interactions broaden and push both valence and conduction states to higher energy.

High energy valence states can act as hole traps and low energy conduction states can act as electron traps. As seen in Fig. 3, intra-molecular distortions, on average, symmetrically broaden valence states and broaden and push conduction states to lower energy, whereas inter-molecular electronic interactions, on average, broaden and push both valence and conduction states to higher energy. As a result, electron trap states are favored by intra-molecular configurational disorder, and hole trap states are favored by inter-molecular electronic interactions. In substituted polymers, such as MEH-PPV, inter-molecular electronic interactions are reduced compared to pristine polymers. Thus, hole traps should be more dominant in pristine PPV and electron traps more dominant in PPVs with long side-chains.

Fig. 4 shows the electron densities (squared molecular orbital amplitude) for selected one electron states. Fig. 4A shows the electron density for the LUMO of the oligomer crystal. This state, like all the other states in the crystal, is delocalized throughout the crystal. By

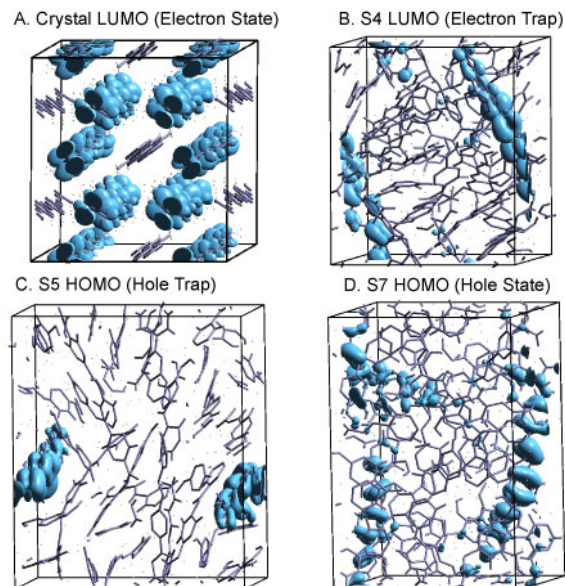


FIG. 4: Calculated electron densities for selected states: (A) the crystal LUMO state; (B) the LUMO level for cluster S4; (C) the HOMO level for cluster S5; and (D) the HOMO level for cluster S7.

contrast, the HOMO and LUMO states in the disordered oligomer clusters are generally localized on individual molecules, whereas states further from the energy gap are often delocalized on more than one oligomer. Fig. 4B shows the LUMO level for cluster S4. This state (see Fig. 2) is separated in energy from the other states in the cluster and lies deep within the energy gap of the corresponding crystal. It is strongly localized on a single oligomer. Fig. 4C shows the HOMO level for cluster S5. This state (see Fig. 2) is also separated in energy from the other states in the cluster, in the energy gap of the corresponding crystal, and strongly localized. Fig. 4D shows the HOMO level for cluster S7. This state (see Fig. 2) is not strongly separated in energy from the other states in the cluster and not as deep into the energy gap of the corresponding crystal as the LUMO level on cluster S4 or the HOMO level on cluster S5. It is delocalized on several oligomers. The deep trap levels in the disordered clusters are usually localized on a single molecule. The S4 LUMO is an example of an electron trap localized on one oligomer, and the HOMO of S5 is an example of a hole trap localized on one oligomer.

In summary, we used a combination of classical molecular dynamics and density functional theory to investigate the role of intra-molecular conformational disorder and inter-molecular electronic interactions on the electronic structure of disordered clusters of poly-*p*-phenylene vinylene (PPV). We found that electron trap states are induced primarily by intra-molecular configurational disorder, while the hole trap states are generated primarily from inter-molecular electronic interactions.

Thin films of PPV consist of small ordered regions, with a local structure similar to that of the crystalline oligomers, separated by disordered regions. In substituted PPVs such as MEH-PPV the side groups separate the conjugated segments of different molecules and reduce inter-molecular electronic interactions compared to pristine PPV. Our model suggests that hole traps should be more dominant in pristine PPV, compared to PPV with long side-chains due to the weak inter-molecular electronic interactions in the latter. Because traps are important in determining electrical transport properties, these results provide strategies to design materials for good electrical transport.

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- [1] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, P. L. Burns, and A. B. Holmes, *Nature* **347**, 539 (1990).
- [2] M. Wohlgenannt, X.M. Jiang, Z.V. Vardeny and R.G. J. Janssen, *Phys. Rev. Lett.* **88**, 197401, (2002); F. Schindler, J.M. Lupton, J. Feldmann, and U. Scherf, *Proc. Natl. Acad. Sci. USA* **101**, 14695 (2004); C. Tanase, P. W. M. Bolm and D. M. de Leenuw, *Phys. Rev. B* **70**, 193202 (2004).
- [3] E. Tutis, I. Batistic, and D. Berner, *Phys. Rev. B* **70**, 161202 (2004); J.G.S. Ramon and E.R. Bittner, *J. Chem. Phys.* **126**, 181101 (2007); L. Liu, D. Yaron, M. Sluch and M. A. Berg, *J. Phys. Chem. B* **110**, 18844 (2006).
- [4] P. F. V. Hutten, J. Wildeman, A. Meetsma, and G. Hadziioannou, *J. Am. Chem. Soc.* **121**, 5910 (1999).
- [5] N. L. Allinger and Y. H. Yuh and J.-H. Lii, *J. Am. Chem. Soc.* **111**, 8551 (1989); J.-H. Lii and N. L. Allinger, *J. Phys. Org. Chem.* **7**, 591 (1994); *J. Comput. Chem.* **19**, 1001 (1998).
- [6] J. W. Ponder, TINKER: Software Tools for Molecular Design, Version 3.8; Washington University School of Medicine, 2000.
- [7] J. P. Perdew, in *Electronic Structure of Solids '91* Edited by P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991), p.11; J. P. Perdew and Y. Wang, *Phys. Rev. B* **45**, 13244, (1992).
- [8] G. Kresse and J. Hafner, *Phys. Rev. B* **47**, 558 (1993); **49**, 14251 (1994); G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 16 (1996); *Phys. Rev. B* **55**, 11169 (1996).
- [9] G. Kresse and J. Joubert, *Phys. Rev. B* **59**, 1758 (1999); P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- [10] D.C. Bott, C.S. Brown, J.N. Winter and J. Barker, *Polymer* **28**, 601 (1987); S. Sasaki, T. Yamamoto, T. Kanbara and A. Morita, *J. Polym. Sci. Part B: Polym. Phys.* **30**, 293 (1992).